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HIGH RESOLUTION ALPHA-SPECTROMETRY FOR RADIUM ANALYSIS THE EFFECTS OF SAMPLE THICKNESS AND FILTER PORE SIZE

by

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ABSTRACT

In the alpha-spectrometric technique for radium isotope analysis, the effects of the barium carrier thickness and pore size of the membrane filter (used for the main Ba-Ra sulphates filtration) on the resolution of the α-energy peaks were investigated. With 0.45 μm Millipore membrane filters, the full width at half maximum (FWHM) for 4.78 MeV alpha-decay peak of Ra-226 decreased from 221.7 keV to 121.3 keV with reduction in barium carrier additions from 320 μg to 20 μg Ba. The resolution further improved to 74.5 keV for 20 μg Ba carrier when 0.2 μm Nucleopore filters were used. There was also a significant decrease (20-50%) in the retention of radon and its daughters compared to their equilibrium concentrations as the barium carrier thickness was reduced.

A correlation study between Ba-133 tracer and Ra-226 isotopes recovery factors gave a recovery factor Ra-226/Ba-133 ratio of 0.93 $\pm$ 0.08 in the main Ba-Ra sulphate precipitate under various pH and sulphate concentration conditions.

Key word: Alpha-spectrometry; Radium isotopes; Resolution.

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L'UTILISATION DE LA SPECTROMÉTRIE ALPHA À HAUTE RÉSOLUTION POUR L'ANALYSE DES ISOTOPES DE RADIUM - LES EFFETS DE L'ÉPAISSEUR DE L'ÉCHANTILLON ET DES DIMENSIONS DES VIDES DU FILTRE

par

T.P. Lim*, N.K. Dave** et N.R. Cloutier***

RÉSUMÉ

Les auteurs ont examiné les effets de l'épaisseur du baryum entraîneur et des dimensions des vides du filtre-membrane (utilisé pour filtrer les principaux sulfates de Ba et de Ra) sur la résolution des pics alpha au cours de l'analyse des isotopes de radium par spectrométrie alpha. Dans le cas des filtres-membranes Millipore de 0,45 µm, la largeur à mi-hauteur (LMII) du pic de 4,78 MeV produit par la désintégration alpha du Ra^{226} s'est abaissé de 221,7 keV à 121,3 keV lorsque l'addition des entraîneurs est tombé de 320 µg à 20 µg. L'utilisation de filtres Nucleopore de 0,2 µm a permis d'améliorer la résolution, qui est passé à 74,5 keV pour 20 µg de baryum entraîneur. La rétention du radon et de ses produits de filiation a baissé considérablement (entre 20 % et 50 %) par rapport aux concentrations d'équilibre à mesure que l'épaisseur de l'entraîneur a été réduit.

Une étude de la corrélation entre le traceur Ba^{133} et les facteurs de récupération du Ra^{226} a donné comme résultat 0,93 ± 0,08 pour le rapport du facteur de récupération Ra^{226}/Ba^{133} dans le précipité composé des principaux sulfates de Ba et Ra avec divers pH et diverses concentrations de sulfates.

Mots-clés: spectrométrie alpha; isotopes de radium; résolution.

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INTRODUCTION

Radium isotopes are frequently monitored in environmental samples associated with uranium mining, milling, fuel processing and power plant operations. For α-emitting radionuclides such as Ra-226, Ra-224 and Ra-223, the α-spectrometric technique using a silicon surface barrier detector provides a rapid method for the simultaneous measurement of their component fractions. There are, however, several spectral interference related problems in separating parent and daughter radionuclides when the overall system resolution is poor as reported in our previous study (1). During that study it was observed that the low resolution (FWHM ~229 keV) was caused by the final sample thickness and the particle size of the barium-radium sulphate crystals.

In the present study, we have further investigated the effects of the deposited sample thickness in terms of Barium carrier additions on:

1) the overall resolution of the system;

2) the analytical recovery factor; and

3) the final equilibrium between Ra and its daughter products.

The effect that the pore size of the membrane filter had on the deposition characteristics of the final precipitate and resolution was also investigated.

In a separate experiment we further investigated the correlation between the recovery of Ba-133 tracer and Ra-226 isotopes in the final Ba-Ra sulphate precipitate over the entire range varying between 0 to 100% recovery which was obtained by altering various controlling parameters such as pH and sulphate concentration in the final precipitating solutions.

METHOD

The technique used here is a modification of our previous method described in detail by Lim et al. (1), and Zimmerman et al. (2), where radium is separated chemically using barium as a carrier and co-precipitated as Ba-Ra sulphates. The final resolution of the system, defined as the full width half maximum (FWHM) of the α-particle spectrum line shape for a given energy peak, depended on the amount of barium carrier added for co-precipitation, particle size of the final precipitate, and its uniformity during deposition.

The amount of barium carrier added causes self-absorption and energy dispersion of α-particles, resulting in broadening of the spectral line shapes (1). Theoretically, by decreasing the amount of the carrier added, the resolution of the α-energy spectra can be improved to a certain extent which is limited by the required analytical recovery factors and is dependent upon the solubility of $BaSO_4$ in the final precipitating solution. The minimum volume of the final solution is the critical parameter in controlling the thickness of the Ba-Ra sulphate deposition as the amount of barium carrier needed to exceed the solubility limit depends on the final volume. The method described here is based on the final volume of approximately 10 mL which contains 5 mL of ammoniacal E.D.T.A. (for complexing the primary precipitate containing Pb, Ba, and Ra sulphates), 1 mL of saturated ammonium sulphate solution, and 3 to 4 mL of glacial acetic acid.

For testing self-absorption in various sample thicknesses, and to achieve a higher resolution, eight samples were prepared in duplicate by spiking each of them with 29.7 Bq of Ra-226 and a known amount of Ba-133 tracer for recovery factor calculations. A known amount of $Ba(NO_3)_2$ carrier as solution was added to each sample containing 320, 120, 90, 70, 50, 30, 25 and 20 mL at 1 μg/mL Barium. The samples were then prepared according to the

following procedure and deposited on the two different membrane filters, Millipore 0.45 μm and Nucleopore 0.2 μm polycarbonate, respectively.

APPARATUS

Millipore filter apparatus (to hold 25 and 45 mm diameter filters):

Millipore filter No. HABP 01500; 0.45 μm;

HABP 04700; 0.45 μm;

Nucleopore polycarbonate 0.20 μm filter with 25 mm diameter;

Magnetic stirrer and stirring bars;

Pipettes (various sizes);

Graduated cylinder (250 mL).

REAGENTS

12 M Hydrochloric acid;

1 M citric acid;

14.3 M ammonium hydroxide;

Ba-133 tracer solution, 65.87 Bq/mL;

Indicator paper pH range 6-9;

Lead nitrate solution: 12.79 g $Pb(NO_3)_2$/L;

Barium nitrate solution: 1.9032 mg $Ba(NO_3)_2$/L = 1 μg/mL Ba;

8 M sulphuric acid;

E.D.T.A., disodium salt in solution: 0.25 M;

Saturated ammonium sulphate solution: 100 g $(NH_4)_2\ SO_4$/L;

17.4 M acetic acid.

ANALYTICAL PROCEDURE

For this study Ra-226 standard solution was prepared using Amersham radium solution which was calibrated against NBS standard. The concentration of the Ra-226 standard solution used was 1188 Bq/L $\pm$ 3.16%. The Ba-133 tracer solution was prepared by diluting stock solution to contain 65.87 Bq/mL of Ba-133 in the working solution.

An aliquot of 25 mL was taken for each test which represented 29.7 Bq of Ra-226 and diluted with distilled water to a final volume of 250 mL. The samples were prepared as follows:

- Add 10 mL of Ba-133 tracer working solution to the above solution and boil the final solution;
- Add 20 mL (1 M) citric acid to the hot solution. While stirring with magnetic stirrers, add concentrated ammonium hydroxide to pH 8-9 (test with pH paper);
- Slowly add 10 mL $Pb(NO_3)_2$ solution, 20 mL $Ba(NO_3)_2$ solution and 5 mL saturated $(NH_4)_2\ SO_4$ to the ammoniacal solution while stirring.

  Note: 5 μg barium carrier in excess was added.
- Using pH meter, and while stirring adjust pH to 0.9 by adding 8 mL of sulphuric acid. Continue stirring until the temperature drops to an ambient temperature. The sulphate precipitate should appear at this stage.

  Note: stirring is very important throughout this procedure to ensure rapid homogeneous precipitation. Cooling using a water bath while stirring will speed up the process.
- Filter the combined sulphates of Pb, Ba and Ra on a millipore HABP 04700 (0.45 μm) filter. Thoroughly rinse the beaker with 10% methanol solution and discard the filtrate;
- Roll the filter with the deposited powder facing inside and transfer it into a 25 mL test tube;
- Add approximately 3 drops of concentrated ammonium hydroxide, 5 mL of 0.25 M E.D.T.A;
- Heat until nearly boiling and shake the test tube vigorously until all the white powder is dissolved into the solution;
- Withdraw the filter slowly along the wall of the test tube to allow drops of solution to drip from the filter back into the tube;

- Discard the filter and no rinsing is necessary (to keep the final volume small).

  Note: To obtain a high recovery factor, ensure that all the precipitate is dissolved in E.D.T.A. solution before discarding the filter paper. It is a good practice to count Ba-133 residue on the filter and filtrate before discarding them.
- Add 1 mL of saturated ammonium sulphate to the ammoniacal E.D.T.A. solution.
- Add 3 mL of concentrated glacial acetic acid;
- Shake vigorously to ensure a homogeneous mixture and leave it standing 10 to 15 min;

  Note: the pH at this stage should be less than 4.8. A faint cloudy precipitate of Ba-Ra sulphate should appear at this stage.
- Filter the Ba-Ra precipitate on a millipore HABP 02500 (0.45 μm) or Nucleopore 0.20 μm polycarbonate filter;
- Rinse the glass tube and filter apparatus with 10% methanol for maximum recovery.
- Remove the filter paper and glue it onto an aluminum planchet with double sticky tape and dry it in a desiccator;
- The planchet is now ready for counting.
- With the above procedure, one sample can be prepared in less than one hour.

For Ba-Ra sulphate correlation study, forty samples were prepared in batches of 10 samples, each containing 270 mBq of Ra-226 and 658.7 Bq of Ba-133 tracer solution. The first batch of 10 samples was precipitated using the standard procedure as described above. The next two batches of 20 samples were precipitated using the same procedure as above, but varying the pH of the final precipitating solution between 3.9 and 6.5. The last batch of 10 samples was precipitated at pH 4.8, but having varying amounts of sulphate

concentrations ranging from 0.05 to 100 mg of ammonium sulphate.

EXPERIMENTAL ARRANGEMENT

The experimental arrangement for α-particle energy spectra consisted of an Ortec ruggedized solid-state surface barrier detector with 300 mm^2 surface area, a preamplifier, amplifier and a bias voltage supply. The detector was positioned at approximately 2 mm from the source and the measurements were performed under vacuum. A 2048 channel Canberra 40 pulse height analyzer was used for data acquisition.

For γ-spectroscopy, a Harshaw type 16MB/6/B 10.2 cm Na(Tl)I γ-probe was used, and the γ-energy spectra were analyzed using a Tracor Northern data acquisition system.

RESULTS AND DISCUSSION

Figures 1 to 3 show the α-spectra of Ra-226 obtained for barium carrier thicknesses varying from 320 to 20 μg. The observed FWHM for various source thicknesses are tabulated in Table 1. From these results, it can be seen that for 0.45 μm Millipore filters, the observed FWHM decreased from 221.7 keV for 320 μg barium to 121.3 keV for 20 μg barium carrier amounts without any consistent trend as the barium carrier thickness was decreased.

The data showed a scattering trend for carrier thicknesses below 50 $\mu g/cm^2$. In this region, factors such as uniformity of the sample thickness and particle size of the final precipitate become dominating. Sill (3) has demonstrated the effects of these parameters by reducing the crystal size of the final precipitate by adding a barium sulphate seeding suspension to the final precipitating solution where he obtained 97% analytical recovery with alpha resolution at FWHM of 60 keV.

In this study we attempted to obtain similar results by decreasing the barium carrier concentration in the final precipitating solution near its

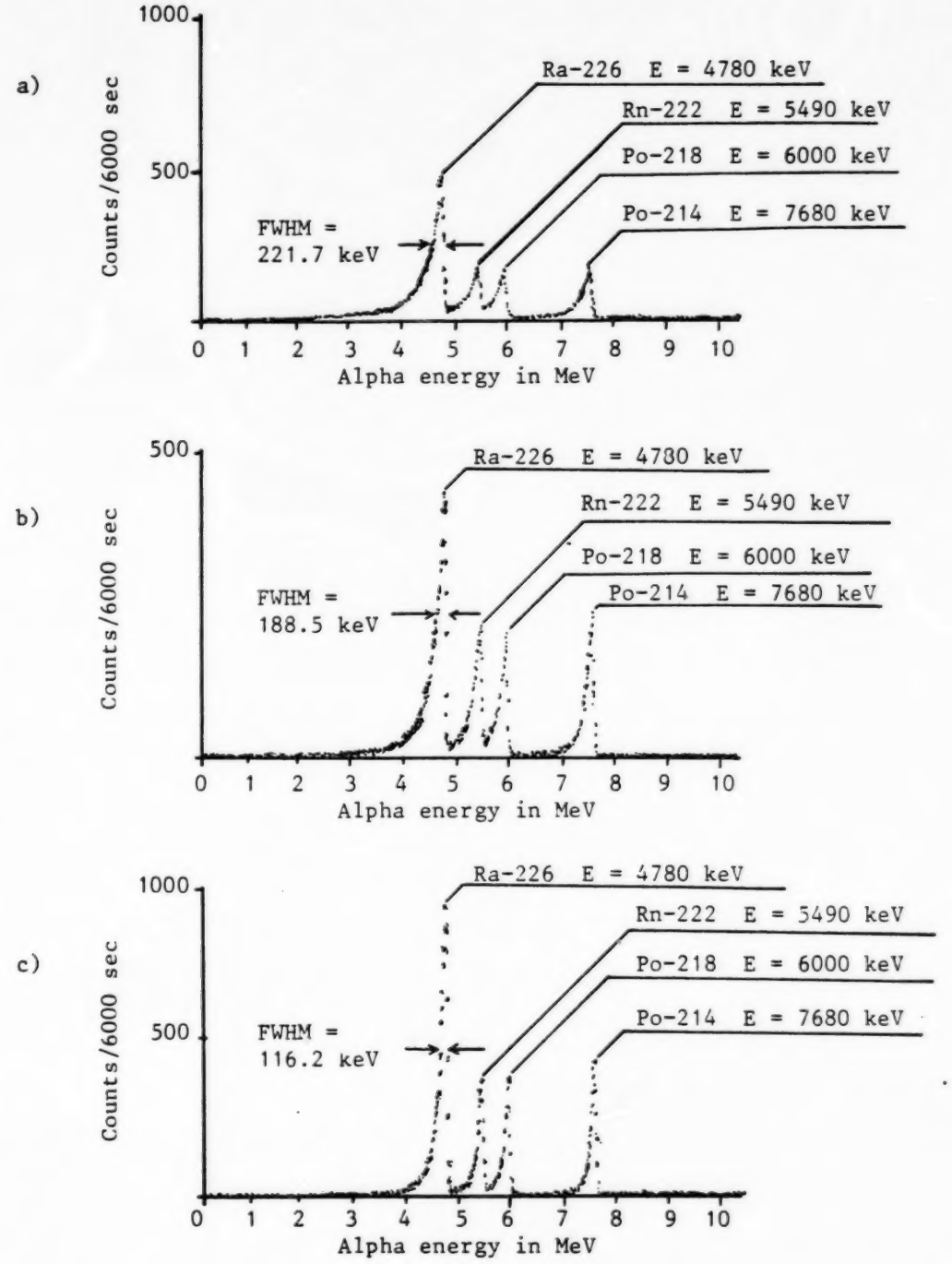

Fig. 1 - Ra-226 alpha energy spectra using an 0.45 µm Millipore filter. Barium carrier added: a) 320 µg; b) 120 µg; c) 90 µg. FWHM = full width half maximum.

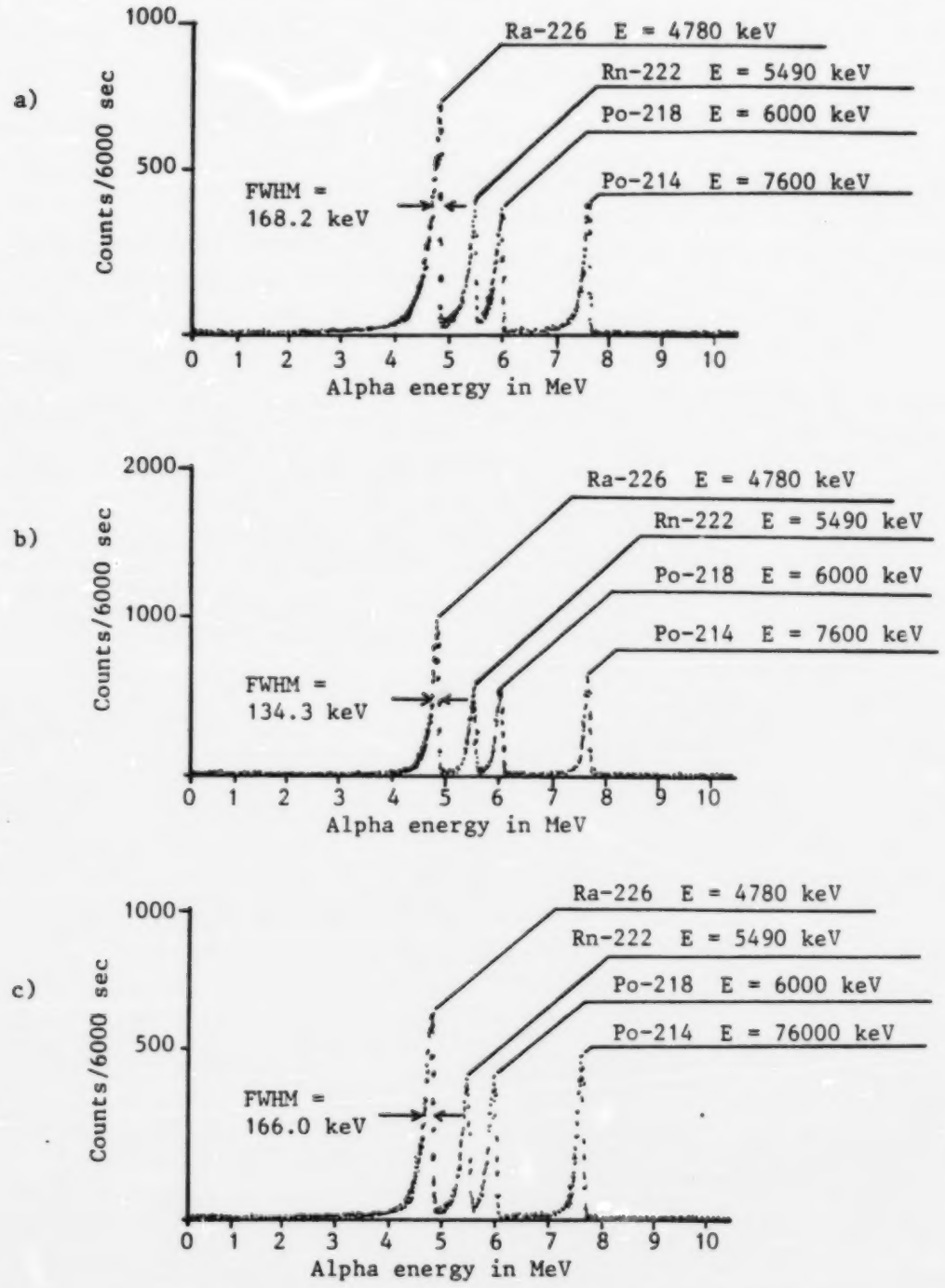

Fig. 2 - Ra-226 alpha energy spectra using 0.45 µm Millipore filter. Barium carrier added: a) 70 µg; b) 50 µg; c) 30 µg. FWHM = full width half maximum.

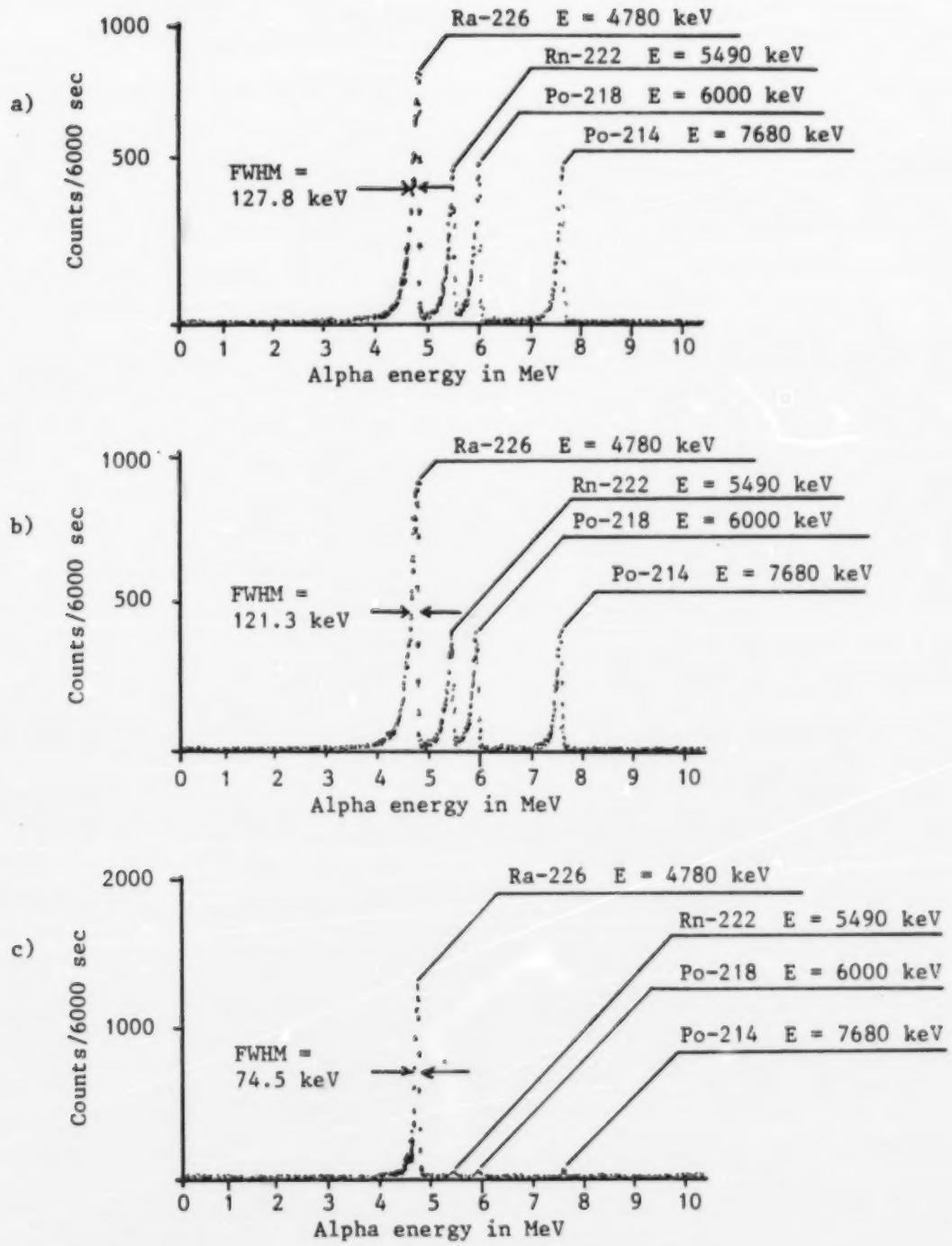

Fig. 3 - Ra-226 alpha energy spectra using 0.45 µm Millipore filter. Barium carrier added: a) 25 µg; b) 20 µg; c) using 0.2 µm Nucleopore filter with 20 µg Ba.

Table 1 - Full width half maximum (FWHM) for Ra-226, 4.78 MeV peak for various amounts of barium carrier added. The diameter of the source = 1.52 cm; area of the source = 1.815 cm^2.

Barium Carrier Added µg	Recovery Factor Ba-133 %	Barium Carrier Thickness µg/cm^2	FWHM keV	Figure No.
	Filter type: Millipore, 0.45 µm HABP 02500			
320	91.3	161.0	221.7	1a
120	56.3	37.2	188.5	1b
90	91.8	45.5	116.2	1c
70	89.4	34.5	168.2	2a
50	98.0	27.0	134.3	2b
30	74.5	12.3	166.0	2c
25	79.8	11.0	127.8	3a
20	84.6	9.3	121.3	3b
250	81.0	111.6	229	*
100	67.5	37.2	229	*
	Filter type: Nucleopore, 0.2 µm polycarbonate			
20	67.4	7.4	74.5	3c

* Data from previous paper (see Ref. 1).

solubility limits, thereby decreasing the particle size of the precipitate, and by creating uniform depositional conditions by providing increased filter resistance. The latter was achieved by using a 0.2 μm Nucleopore polycarbonate membrane filter which provided about three times higher resistance to liquid filtration than the 0.45 μm Millipore membrane filters as the variation in the pore size distribution of the former is less. The α-spectra for 0.45 μm Millipore and 0.2 μm Nucleopore filters with 20 μg barium carrier are shown in Figure 3. The FWHM decreased from 121.3 KeV for 0.45 μm Millipore to 74.5 keV for 0.2 μm Nucleopore filters. For comparison purposes, Figures 4 and 5 show, respectively, the improvements in the energy resolution for the two filter types.

Figure 4(a) shows the resolution (221.7 keV) achieved by using a 0.45 μm Millipore filter and 320 μg barium carrier addition. Figures 4(b) and 5(a) show the resolution (74.5 keV) obtained with a 0.2 μm Nucleopore filter and 20 μg barium carrier. Figures 4(c) and 5(c) show the resolution (67.0 keV) obtained for Rn-222 peak of a residual spectrum of Ra-226 daughters attached to the detector surface after counting a high activity (approximately 36 Bq) Ra-226 source for 2 hours. The source was then removed, the sample chamber evacuated and counted for 60,000 sec for the residual activity on the detector.

The FWHM of the residual spectrum (67.0 keV) is probably the best instrumental resolution for the present sample detector geometry. Such narrow residual spectra are often encountered in this type of counting arrangements where the detector surface is exposed to attachment or impingement from energetic decay products recoil.

In α-spectra analysis care should be exercised to keep the detector surface contamination free and to subtract any residual spectral contributions from the detector surface.

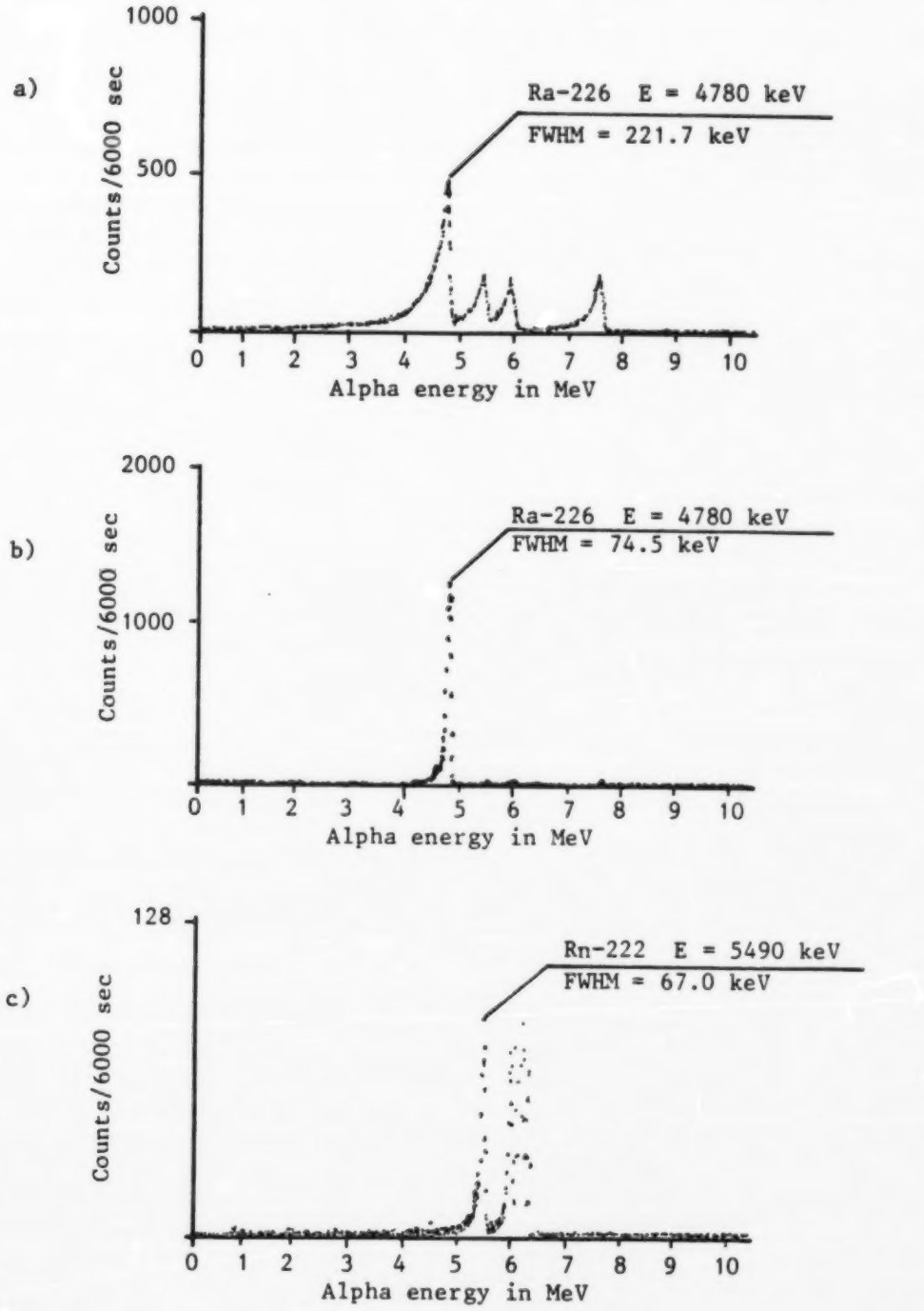

Fig 4 - Comparison of alpha spectra obtained by: a) using 320 µg Ba carrier on 0.45 µm Millipore filter; b) using 20 µg Ba carrier on 0.20 µm Nucleopore filter; c) background counts (residual spectra) of Ra-226 daughters impinged on the surface of the detector.

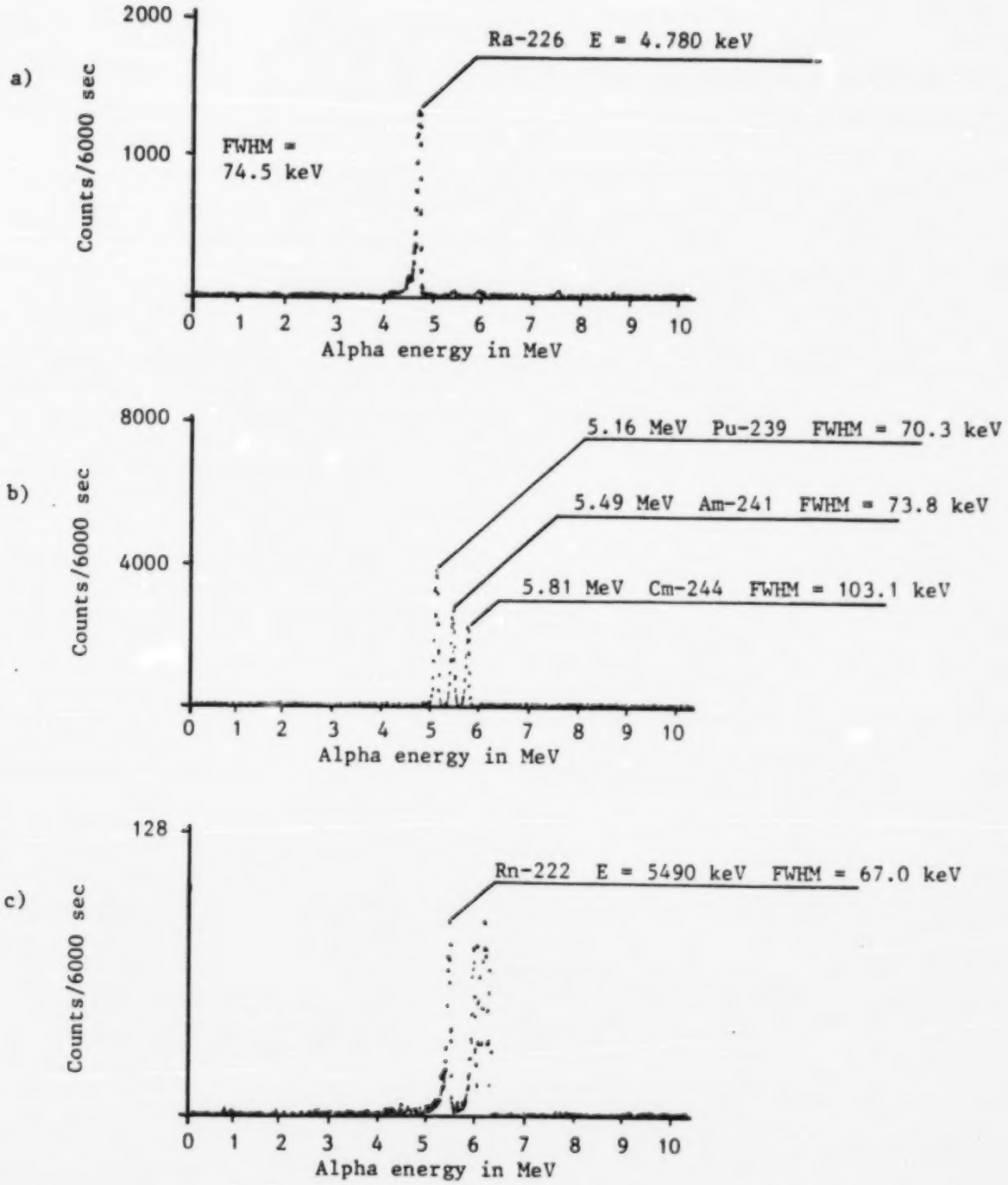
a)
2000
1000
Counts/6000 sec
Ra-226 E = 4.780 keV
FWHM =
74.5 keV
0 1 2 3 4 5 6 7 8 9 10
Alpha energy in MeV
b)
8000
4000
Counts/6000 sec
5.16 MeV Pu-239 FWHM = 70.3 keV
5.49 MeV Am-241 FWHM = 73.8 keV
5.81 MeV Cm-244 FWHM = 103.1 keV
0 1 2 3 4 5 6 7 8 9 10
Alpha energy in MeV
c)
128
Counts/6000 sec
Rn-222 E = 5490 keV FWHM = 67.0 keV
0 1 2 3 4 5 6 7 8 9 10
Alpha energy in MeV

Fig. 5 - Comparison of alpha spectra obtained by: a) using a 0.2 μm Nucleopore filter with 20 μg Ba-carrier; b) commercially electrodeposited mixed source; c) shadow spectrum of Ra-226 daughters.

Figure 5(b) shows the α-spectrum and resolutions obtained for various peaks from a commercially electro-deposited source (Amersham) using mixed radionuclides Pu-239, Am-241 and Cm-244. The best resolutions obtained for 5.16 MeV Pu-239, 5.49 MeV Am-241, and 5.81 MeV Cm-244 α-peaks were respectively, 70.3, 73.8, and 103.1 keV.

It is readily seen from these results that by depositing the final precipitate on 0.2 μm Nucleopore polycarbonate membrane filters, alpha resolution of the system could be considerably improved to its practical limits without much loss in the analytical recovery factors ranging between 67 to 85% (Table 1).

The effect of the high resolution is clearly demonstrated in Figures 6 to 9 obtained from uranium tailings porewater samples containing Ra-223, Ra-224 and Ra-226 isotopes. For comparison purposes, Figure 9(c) also shows Ra-226 spectrum obtained with an 0.2 μm Nucleopore filter and 20 μg barium carrier. Note the resolution of 4.602 MeV (5.55%), and 4.785 MeV Ra-226 peaks, similar to those described by Sill (3).

From Figure 9 it is evident that although there is a clear separation of Ra-226 peaks from those of Ra-223 and Ra-224, component resolutions among Rn-222 (5.490 MeV), Ra-223 (5.61, 5.71 and 5.75 MeV), and Ra-224 (5.45 and 5.68 MeV) peaks is not possible because of spectral interference. Thus, in a sample containing all three isotopes, Ra-226 can be measured directly, but the presence of the other two isotopes can only be inferred qualitatively. Indirect determinations of Ra-223 and Ra-224 from their daughter products (Po-215 for Ra-223), and (Po-212 for Ra-224) which are clearly resolved (as shown in Figure 9) can be accomplished after a certain ingrowth period provided appropriate corrections are made for the loss of radon isotopes from the sample. Table 2 shows the equilibrium ratios for Rn-222/Ra-226, and Po-218/Rn-222 for Ra-222, and Po-214/Rn-222 for Ra-226 isotope after an ingrowth

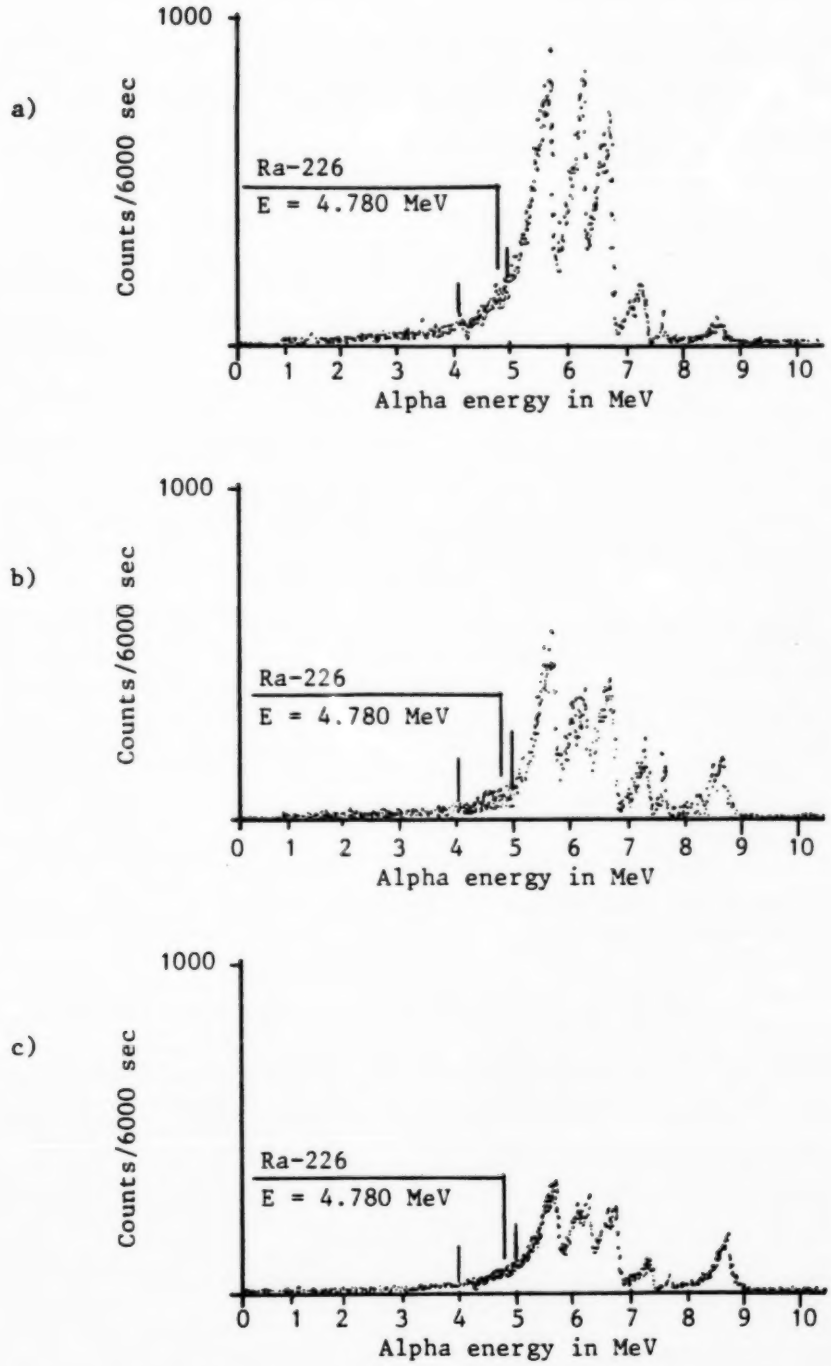

Fig. 6 - Alpha spectra of radium family deposited on 0.45 µm Millipore filter: a) with 300 µg Ba-carrier; b) with 40 µg Ba-carrier counted ø day after separation; c) same as b) but counted 2-days later.

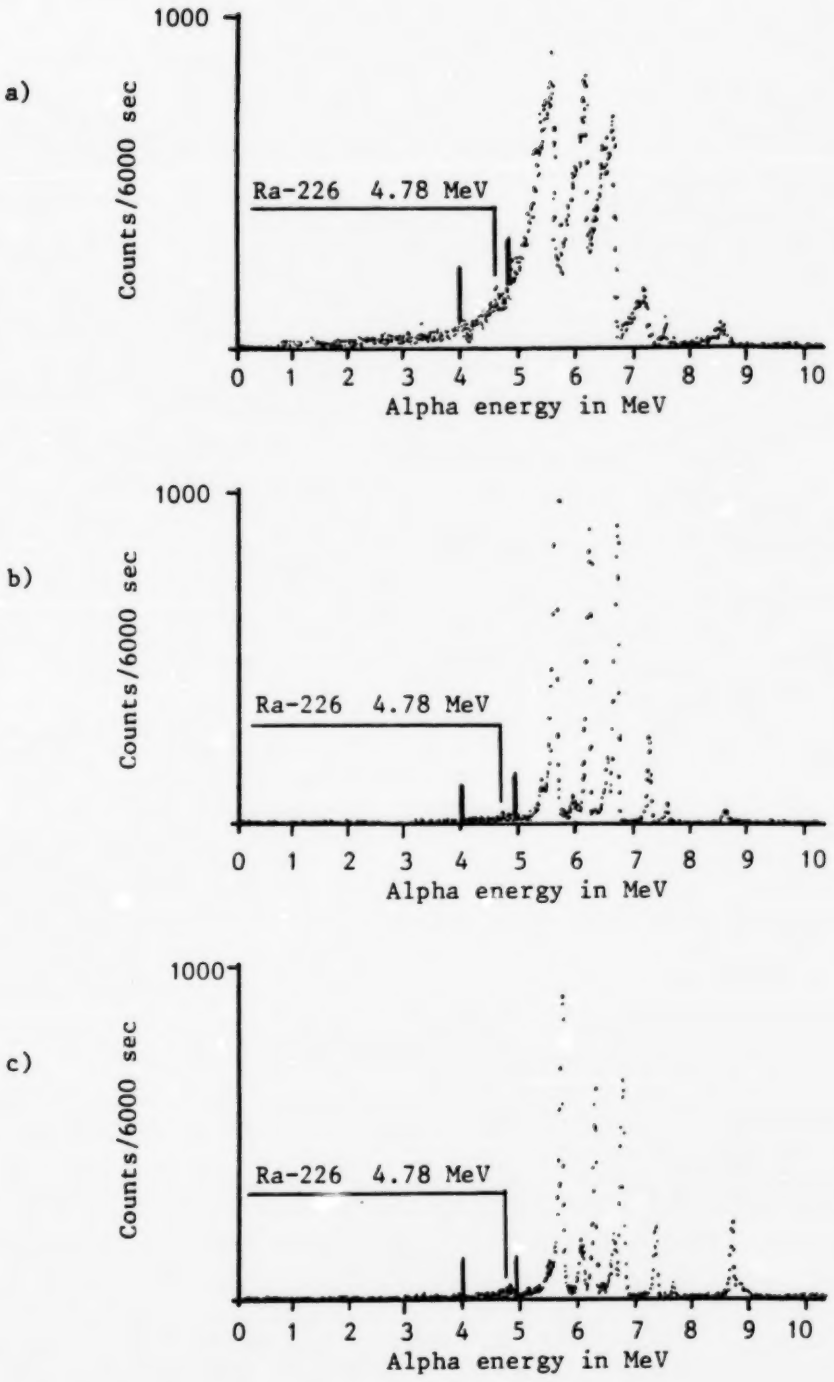

Fig. 7 - Alpha spectra of radium family: a) deposited on 0.45 µm Millipore filter with 300 µg Ba-carrier; b) deposited on 0.2 µm Nucleopore filter with 40 µg Ba-carrier counted ∅ day after separation; c) same as (b) recounted 2-days later.

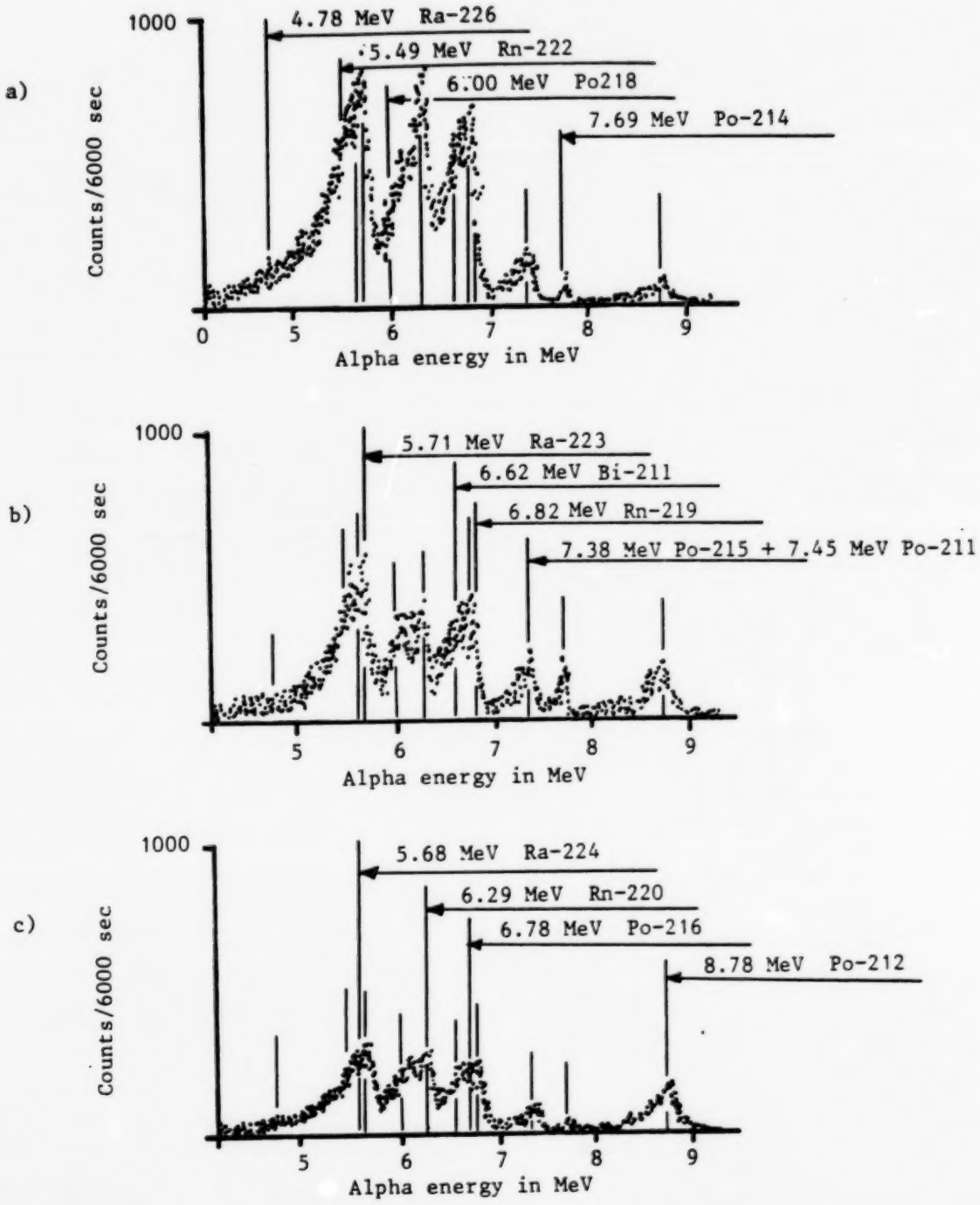

Fig. 8 - Expanded alpha spectra of radium family deposited on 0.45 µm Millipore filter: a) with 300 µg Ba-carrier; b) with 40 µg Ba-carrier counted at ϕ day after separation; c) same as (b) recounted 2-days later.

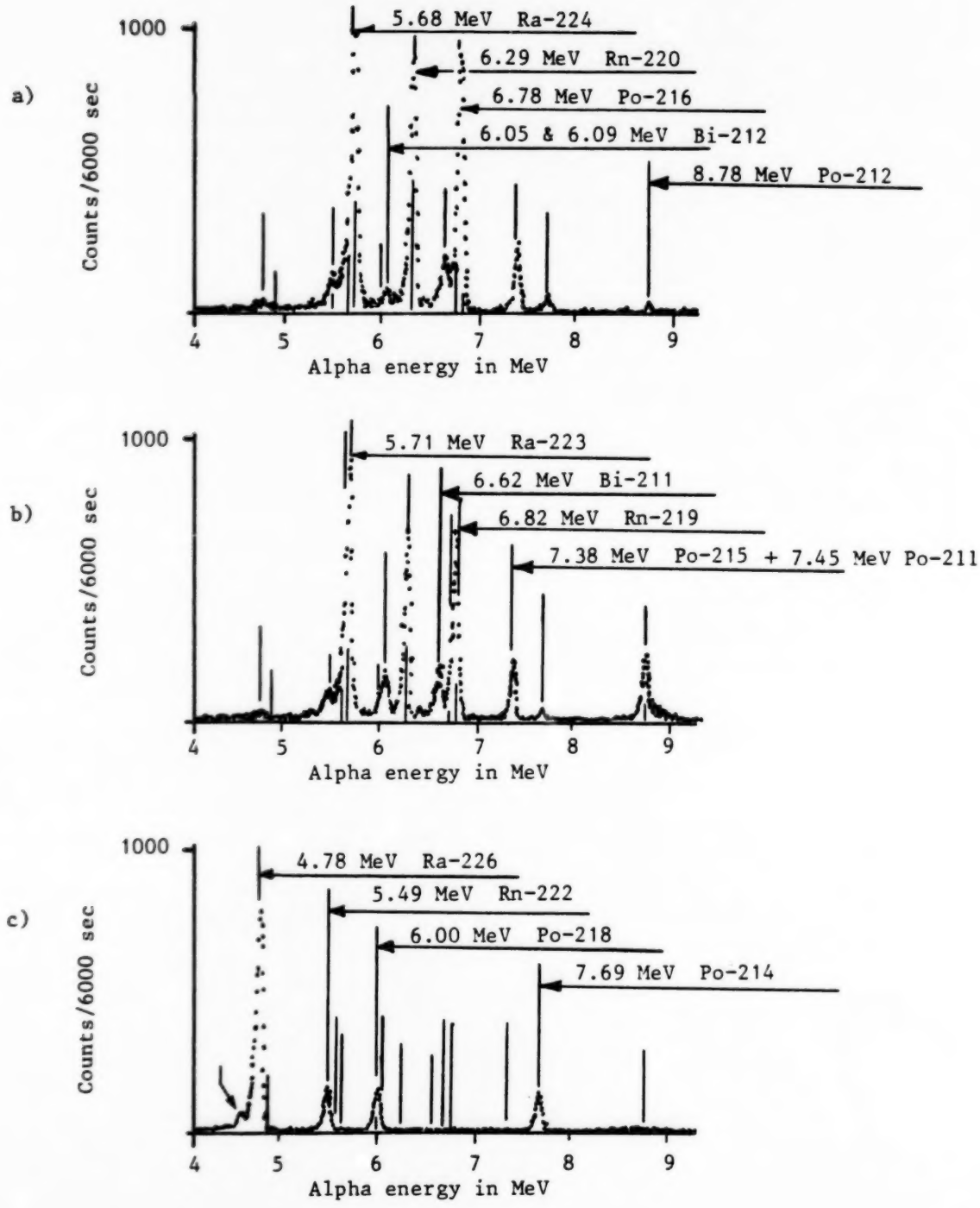

Fig. 9 - Expanded alpha spectra deposited on 0.2 µm Nucleopore filter: a) radium family with 40 µg Ba-carrier counted at ϕ day after separation; b) same as (a) recounted 2-days later; c) Ra-226 spectrum only.

Table 2 - Equilibrium ratio between Ra-226 and its daughter isotopes: Ra-222, Po-218 abd Po-214. Time t = 60 days after radium separation. Expected equilibrium ratio = 100%.

Sample No.	FWHM (keV)	Rn-222/Rn-226 (%)	Po-218/Rn-222 (%)	Po-214/Rn-222 (%)	
1	221.7	106.1	77.1	84.7	
2	120.0	84.0	100.0	96.4	
3	76.0	72.0	93.1	95.9	$\bar{X}$=94.8
4	67.0	55.0	92.7	90.8	σ=3.3

Note: Sample 1 - Ra-226 standard solution precipitated on 0.45 μm Millipore filter; barium thickness = 258.2 $\mu g/cm^2$.

Sample 2 - Ra-226 standard solution precipitated on 0.22 μm Millipore filter; barium thickness = 13.32 $\mu g/cm^2$.

Sample 3 - Ra-226 standard solution precipitated on 0.2 μm Nucleopore polycarbonate filter; barium thickness = 12.68 $\mu g/cm^2$.

Sample 4 - Ra-226 standard solution precipitated on 0.2 μm Nucleopore polycarbonate filter; barium thickness = 7.25 $\mu g/cm^2$.

period of 60 days.

It can be seen here that with the decrease in the barium carrier concentration, there is a significant loss of radon gas from the sample with only 55% of the equilibrium concentration retained for a sample carrier thickness of 7.25 $\mu g/cm^2$. The loss of radon gas is caused by the decrease in the diffusion path related to crystal size and attenuation of the recoil radon atoms as the carrier thickness is reduced. On the other hand, the equilibrium ratio between radon and its daughter products is close to 95% for all samples having resolution between 67 to 120 KeV, and sample thickness 7.25 to 13.32 $\mu g/cm^2$. For samples containing a higher concentration of barium carrier (~258.2 $\mu g/cm^2$, FWHM = 221.7 keV), the observed ratio between radon and daughter products is less than 100% which was caused by the poor resolution of Ra-226, Ra-222 and Po-218 peaks as the spectral overlap was significant (see Figure 1).

For a given sample, the measured retention ratio for Rn-222/Ra-226 at equilibrium can be used to correct for daughter activities in calculating Ra-223 and Ra-224 from their ingrown daughter concentrations. Alternatively, in a sample containing Ra-223 and Ra-224 isotopes, their activities can also be determined as follows:

1. At the time $t=t_o$ (~0), immediately following the separation of radium isotopes from their parents, determine the combined activity, X, of Ra-223 and Ra-224 from their integrated decay peaks (5.45 to 5.71 MeV), such that:

$$A\ C_{Ra\text{-}223}(0) + B\ C_{Ra\text{-}224}(0) = X\ (Bq) \text{ at } t=t_o \qquad \text{Eq 1}$$

where, A = activity fraction of Ra-223 at $t=t_o = e^{-\lambda_1 t_o}$

B = activity fraction of Ra-224 at $t=t_o = e^{-\lambda_1' t_o}$

$C_{Ra\text{-}223}(0)$ = activity of Ra-223 at t=0

$C_{Ra\text{-}224}(0)$ = activity of Ra-224 at t=0, and

λ_1, and λ_1' are decay constants for Ra-223 and Ra-224, respectively.

It is assumed in the above expression that the activity of ingrown Rn-222 daughters from the Ra-226 isotope was negligibly small for the short counting period.

2. After a certain ingrowth period of daughters, at time $t=t_g$, determine the activity ratio of Po-215/Po-212 as:

$$\frac{\text{Po-215 } (t_g)}{\text{Po-212 } (t_g)} = Y \qquad \text{Eq 2}$$

where, the activities of Po-215 and Po-212 at $t=t_g$ are given by:

$$\text{Po-215}(t_g) = D\ C_{\text{Ra-223}}(0)$$

$$\text{Po-212}(T_g) = F\ C_{\text{Ra-224}}(0) \qquad \text{Eq 3}$$

where, D and F are expressed in terms of decay constants as:

$$D = \frac{\lambda_{\text{Po-215}}}{\lambda_{\text{Ra-223}}} \left(\sum_{n=1}^{3} a_{3n}\ e^{-\lambda_n t_g}\right) \qquad \text{Eq 4}$$

for Ra-223 series, and

$$F = \frac{\lambda'_{\text{Po-212}}}{\lambda'_{\text{Ra-224}}} .Br \left(\sum_{n=1}^{6} a_{6n}\ d^{-\lambda' n t_g}\right) \qquad \text{Eq 5}$$

For Ra-224 series,

where, Br = branching ratio (0.64) for Bi-212 to Po-212, and

$$a_{mn} = \frac{\lambda_1\ \lambda_2 \ldots \lambda_{m-1}}{(\lambda_m-\lambda_n)(\lambda_{m-1}-\lambda_n)\ldots(\lambda_{m-r}-\lambda_n)(\lambda_2-\lambda_n)(\lambda_1-\lambda 1_n)} \qquad \text{Eq 6}$$

where, $m>n$ and $m-r \neq n$.

$$a_{mm} = \frac{\lambda_1\ \lambda_2 \ldots \lambda_{m-1}}{(\lambda_{m-1}-\lambda_m)(\lambda_{m-2}-\lambda_m)\ldots(\lambda_1-\lambda_m)} \qquad \text{Eq 7}$$

for $m = n$.

$\lambda_1, \lambda_2 \ldots \lambda_n$ = decay constants of Ra-223, Rn-219 and Po-215, etc.

$\lambda'_1 \ldots \lambda'_n$ = decay constants of Ra-224, Rn-220...Po-212, etc.

Solving Equations 1 to 3 we have:

$$C_{\text{Ra-223}}(0) = \frac{X.Y.F}{(AYF + BD)} \qquad \text{Eq 8}$$

and, $$C_{Ra\text{-}224}(0) = \frac{X.D}{(AYF + BD)} \qquad \text{Eq 9}$$

Thus, the concentrations of Ra-223 and Ra-224 can be obtained by measuring parameters X and Y and A, B, D and F.

It was assumed in the above derivations that there was no significant difference in the retention characteristics of various radon and their daughter products for the three radium isotopes. Use of computerized models such as those developed by Wätzig, et al. (4), Westmeier (5), and Williams (6) for complex α-spectra could further the analytical capabilities of the present high resolution technique.

BARIUM-RADIUM RECOVERY

Table 3 gives the calculated recovery factors for Ba-133 and Ra-226, true and corrected Ra-226 counts at 100% recovery for 6000 sec. The recovery factors for Ra-226 were calculated using the measured value of the instrumental efficiency factor, ε = 0.224 and source disintegration per minute (dpm) = 22.2, equivalent to total counts per 6000 sec = 497. The observed frequency distributions for Ba-133 and Ra-226 recovery factors are plotted in Figure 10. Figure 11 shows the correlation between the observed Ra-226 counts and Ba-133 recovery factors with a linear relationship of the form:

Y (Ra-226 counts/6000 sec) = 4.57 x (% Ba-133 recovery)

with the coefficient of regression r^2 = 0.98 and standard deviation of the slope = 0.05.

Also shown in Table 3 and Figure 11, are the observed and calculated Ra-226 counts at 100% recovery (curve 'D'). Note that the average Ra-226 counts calculated for 100% recovery were 465 $\pm$ 44 compared to the expected value of 497, the difference being of no statistical significance ($p > 0.05$). Figure 12 shows the correlation between the two calculated recovery factors for Ra-226 and Ba-133. The average value of the Ra-226/Ba-133 recovery ratio

Table 3 - Comparisons between Ba-133 and Ra-226 recovery factors and the observed (true) and Ra-226 counts at 100% recovery. Ra-226 recovery factors were calculated using the instrumental efficiency factor ε=0.224, and true counts = 497.5.

Sample No.	Remark	Recovery Ba-133 %	Ra-226 Counts/ 6000 s	100% Ra-226 Counts/ 6000 s	Recovery Ra-226 %	Recovery Ratio %Ra/%Ba
1	Std. procedure	71.6	382	534	76.8	1.07
2	Std. procedure	90.4	454	502	91.3	1.01
3	Std. procedure	90.4	408	451	82.0	0.91
4	Std. procedure	90.5	400	442	80.4	0.89
5	Std. procedure	87.8	393	447	79.0	0.90
6	Std. procedure	86.8	406	468	81.6	0.94
7	Std. procedure	87.0	391	450	78.6	0.90
8	Std. procedure	85.0	371	436	74.6	0.88
9	Std. procedure	90.0	413	459	83.0	0.92
10	Std. procedure	86.7	384	443	77.2	0.89
11	Prec. at pH=5.90	76.2	369	484	74.2	0.97
12	Prec. at pH=5.45	81.0	404	499	81.2	1.00
13	Prec. at pH=4.98	92.4	420	455	84.5	0.91
14	Prec. at pH=4.48	88.7	347	391	69.8	0.79
15	Prec. at pH=3.95	97.6	385	395	77.4	0.79
16	Prec. at pH=5.98	89.8	390	434	78.4	0.87
17	Prec. at pH=5.25	87.9	389	443	78.2	0.89
18	Prec. at pH=4.99	99.3	462	465	92.9	0.94
19	Prec. at pH=5.30	97.5	416	427	83.7	0.86
20	Prec. at pH=4.56	68.8	329	478	66.2	0.96
21	Prec. at pH=4.68	24.4	98	402	19.7	0.81
22	pH=1.18; pH=5.5	77.0	374	486	75.2	0.98
23	pH=3.42; pH=6.5	0.0	6	465	1.2	-
24	pH=3.38; pH=6.0	0.0	2	465	0.4	-
25	pH=3.3; pH=5.5	67.3	312	464	62.7	0.93
26	pH=3.25; pH=5.25	83.1	376	452	75.6	0.91
27	pH=3.3; pH=5.0	79.4	350	441	70.4	0.89
28	pH=3.4; pH-4.8	68.2	331	485	66.6	0.98
29	pH=3.0; pH=6.5	0.0	2	465	0.4	-
30	pH=3.42; pH=4.8	80.0	331	414	66.6	0.83
31	Final+0.05mg Amm. Sul	0.0	2	465	0.4	-
32	Final+50mg " "	0.0	2	465	0.4	-
33	Final+21mg " "	0.0	1	465	0.2	-
34	Final+125mg " "	13.7	80	583	16.1	1.17
35	Final+115mg " "	72.2	373	517	75.0	1.04
36	Final+75mg " "	56.3	292	519	58.7	1.04
37	Final+2mg " "	0.0	3	465	0.6	-
38	Final+50mg " "	0.0	2	465	0.4	-
39	Final+75mg " "	67.0	341	509	68.6	1.02
40	Final+100mg " "	74.0	371	501	74.6	1.01
			Average:	464.9		0.93
			Std. Dev:	44		0.08

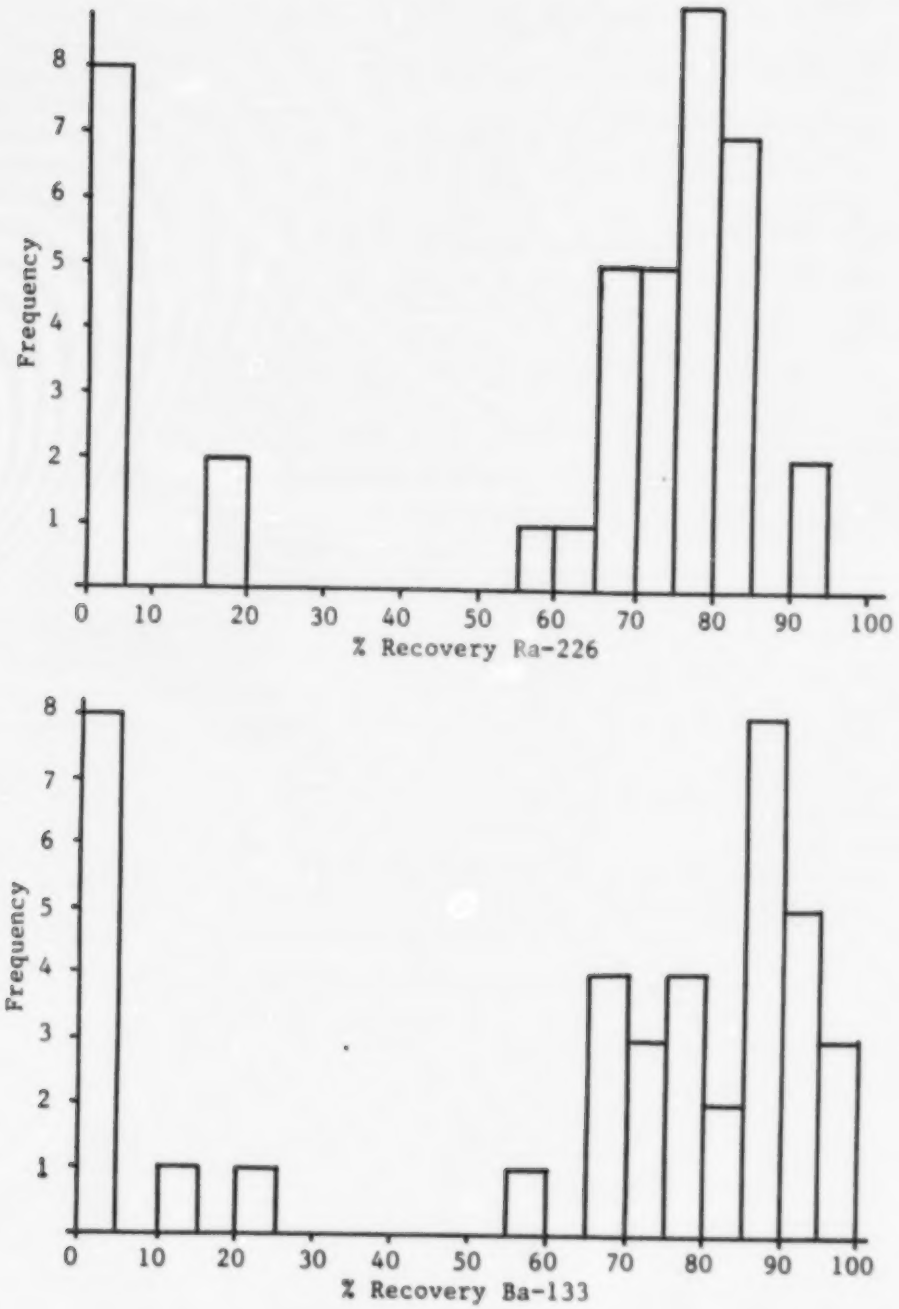

Fig. 10 - Frequency distribution of Ba-133 and Ra-226 recovery factors.

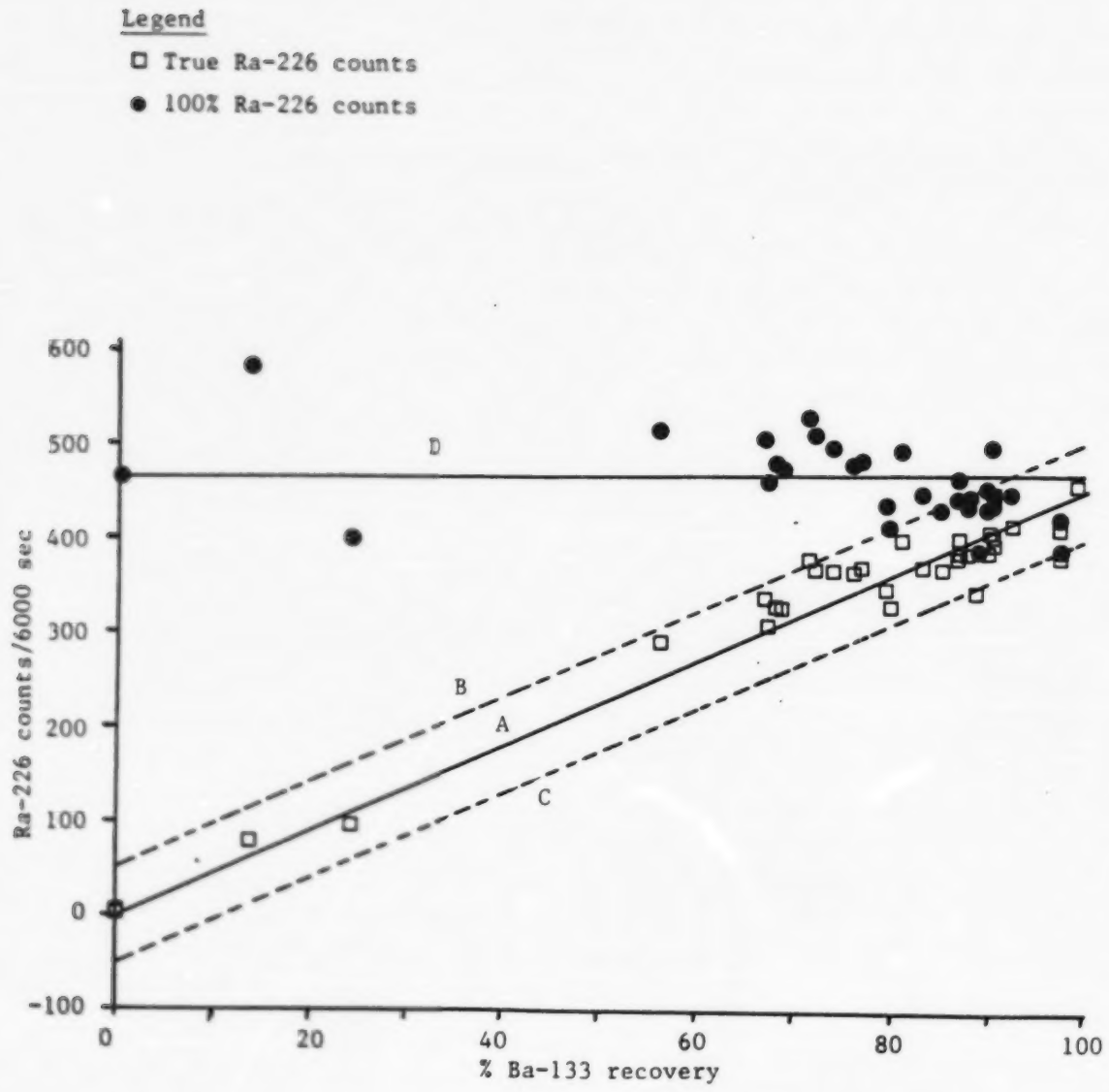

Fig. 11 - Correlation between the observed Ra-226 counts and Ba-133 recovery factor curve (A) with 95% confidence limits (curves B and C). Curve D is the calculated Ra-226 counts at 100% efficiency.

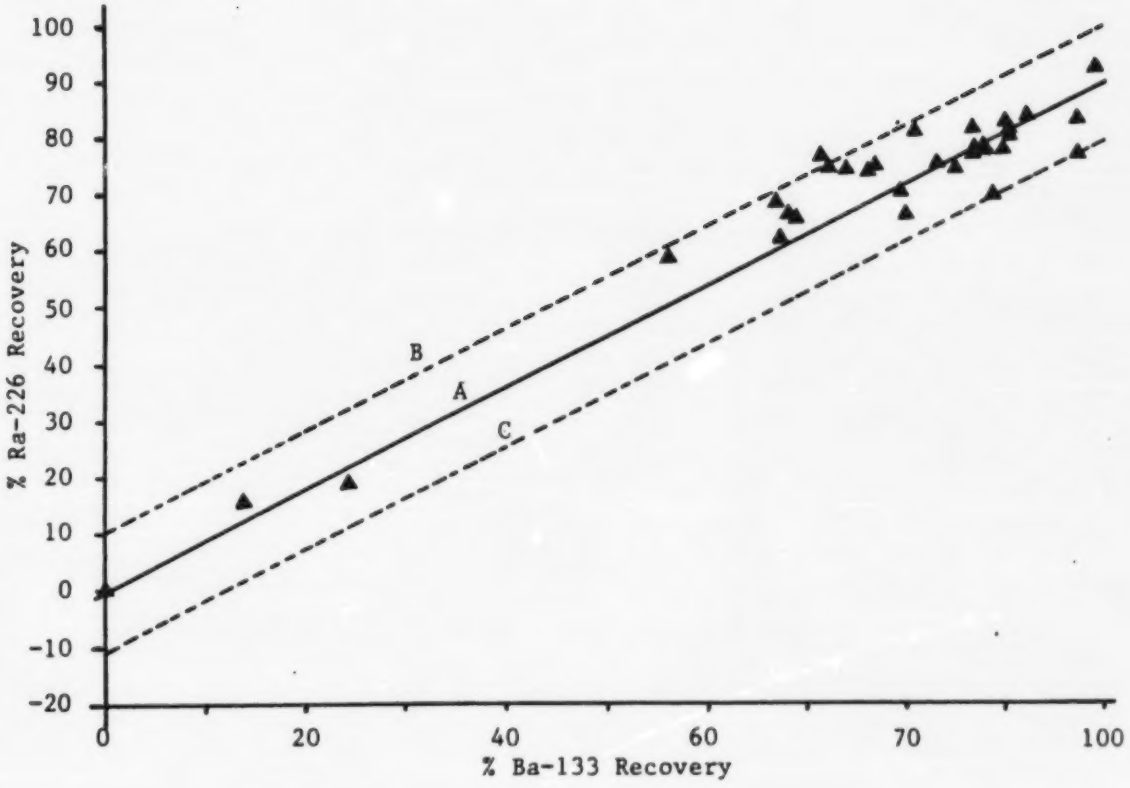

Fig. 12 - Correlation between the actual Ra-226 and Ba-133 recovery factors with 95% confidence limits Curve A, 95% confidence limits Curve B and C.

was calculated as 0.93 ± 0.08 which was statistically not different to the expected value of 1.0 ($p > 0.05$). In the final $BaSO_4$ precipitation procedure, it was aimed at varying the overall recovery of Ba and Ra sulphates over a wide range by adjusting the controlling parameters such as pH and sulphate concentrations, but the final recovery was always high (>60%) except for eight samples where it was zero and for two samples where it varied from 10 to 30%. No attempt was made to vary the barium carrier concentration to obtain different recovery factors as such was not the case in the routine analytical procedure where the carrier concentration was always constant. As seen from the data no systematic trends between low and high recoveries were identifiable.

It can thus be stated from present results that by using a chemically different isotope as a tracer (Ba-133) to measure chemical yield of Ra isotopes, the correlation between the two can only be expressed within a statistical uncertainty of approximately 9%. As Sill (3) has pointed out, better correlation between these two atoms differing in ionic radii and chemical characteristics cannot be expected to the same degree as in the case with similar isotopic tracers. For Ra-226 analysis, however, there are no other radium isotopes with reasonable half-lives that can be used as tracers.

CONCLUSIONS

This study clearly demonstrated that the α-resolution of the system can be improved by a factor of 3 by decreasing the barium carrier concentration to 20 μg, and using a 0.2 μm Nucleopore membrane filter without much loss in chemical recovery. The overall effect was to reduce the broadening of the α-spectral peaks because of self-absorption of α-particles within the deposited barium sulphate and its crystalline matrix. There was also a significant decrease in the retention of radon and its daughters with decrease of barium

carrier.

Correlation between Ba-133 and Ra-226 isotopic recovery factors showed that for the main Ba-Ra sulphate precipitates, the recovery factors between these two chemically different atoms can only be expressed within a statistical uncertainty of ±9%.

REFERENCES

1. Lim, T.P. and Dave, N.K., "A rapid method of Ra-226 analysis in water samples using an alpha-spectroscopic technique"; CIM Bull. vol 74, No. 833, p. 97; September 1981.

2. Zimmerman, J.B. and Armstrong, V.C., "The determination of Ra-226 in uranium ores and mill products by alpha-energy spectra"; Division Report MRP/MRL 76-11, CANMET, Energy, Mines and Resouces Canada; 1971.

3. Sill, C.W., "Determination of radium-226 by high resolution alpha-spectrometry"; Report DE83-014 959, EG&G Inc., Idaho Falls, Idaho, U.S.A.; 1983.

4. Wätzig, W. and Westmeier, W., "Alfun - a program for the evaluation of complex alpha-spectra"; Nuclear Instrum & Methods, vol. 153, p. 517; 1978.

5. Westmeier, W., "Computerized analysis of alpha-particle spectra"; Int J Appl Rad & Isotopes, vol. 35, No. 4, pp. 263-270; 1984.

6. Williams, R.L., "A computerized alpha-particle-spectrometry system for the analysis of low-level thorium, uranium, plutonium and americium fractions"; Int J Appl Rad & Isotopes, vol. 35, No. 4, pp. 271-277; 1984.